

DESCRIPTION

COMPOSITE COATED ZINC-CONTAINING PLATED STEEL MATERIAL
SUPERIOR IN CORROSION RESISTANCE, BLACKENING RESISTANCE,
5 COATING ADHESION, AND ALKALI RESISTANCE

TECHNICAL FIELD

The present invention relates to a composite coated
plated steel material comprised of a plated steel
10 material used unpainted or painted and given superior
corrosion resistance, blackening resistance, coating
adhesion, and alkali resistance. More particularly, the
present invention relates to a completely chrome-free
composite coated zinc-containing plated steel material
15 imparting superior corrosion resistance, blackening
resistance, coating adhesion, and alkali resistance to a
shaped article made using a zinc-containing plated steel,
for example, a shaped article used for a roof, wall, or
other building member or a member of an automobile,
20 machine, household electrical appliance, etc., or a sheet
coil.

BACKGROUND ART

Zinc-containing plated steel materials and other
plated steel materials are being widely used as building
25 materials and members of automobiles, household
electrical appliances, etc. due to the high corrosion
preventing function of the plating layer metal. However,
in plated steel materials, the phenomenon sometimes
arises of oxidation due to the salts and other
30 electrolytes contained in the air and the oxygen and
moisture present in high temperature, humid environments
and consequent formation of white rust and corrosion.
Further, in certain environments of a high temperature
and humidity, the phenomenon arises of the plated steel
35 material discoloring and appearing to be black. Both
these phenomena are due to the deterioration of the
plating layer metal and are sometimes considered a

problem from the viewpoint of quality and aesthetics when the material is assembled into the above various products.

5 Further, even when used painted, the penetration of oxygen or moisture sometimes leads to the peeling of the paint film due to the formation or buildup of corrosion products at the plating layer under the paint film. Sometimes a problem is caused in terms of aesthetics and practical use.

10 Further, sometimes a plated steel material is cleaned by an alkaline degreasing agent after being shaped. In this case, if the material is not durable against alkali, it will discolor or will end up corroding early during use.

15 As means for preventing such corrosion, blackening, or paint peeling of plated steel materials, in the past the surfaces have been treated by various techniques bringing chrome-containing treatment solutions, such as chromic acid-chromate or phosphoric acid-chromate
20 solutions, into contact with the surfaces of the plated steel materials. By forming what is generally called a "reaction type chromate coating" on the surface of a plated steel material, the above problems are avoided. The chromate coatings obtained by these treatments are
25 mainly comprised of trivalent chrome. While the amount of leaching of the particularly toxic hexavalent chrome is small, the corrosion prevention property cannot be said to be sufficient. In particular, when the damage to a coating due to shaping or scratches reaching the base
30 iron is large, the plated steel material drops in corrosion resistance.

On the other hand, in coating type chromate treatment where a treatment solution containing hexavalent chrome is coated by a roll coater etc. on a
35 material and dried, the coating formed will contain a large amount of hexavalent chrome. Therefore, even if the chromate coating is damaged due to being worked or

scratches etc., the material will have superior corrosion resistance, but sometimes hexavalent chrome will leach out from the chromate coating. Chromate treatment coatings containing hexavalent chrome have a detrimental effect on the human body upon buildup due to their toxicity. As explained above, the coating easily leaches out by nature. Therefore, there can be said to be the problem in terms of environmental protection of the environmental load substances moving outside the system.

In this way, the chromate treatment performed on plated steel materials in the past for the purpose of preventing the formation of white rust is becoming an issue in terms of safety and environmental impact due to the hexavalent chrome. To solve this problem, technology for replacing chromate treatment has been studied.

As a publication describing art replacing chromate by coating a chromate-free treatment solution on the surface of a plated steel material, JP 2002-332574 A may be mentioned. This publication proposes the art of coating a treatment solution containing zirconium carbonate complex ions and vanadyl ions, dimercaptosuccinic acid, etc. and heating it to dry to form a coating of a dense three-dimensional structure and obtain a superior corrosion resistance due to the high ability of adsorption on the surface metal. Further, JP 2002-030460 A describes metal surface treatment agents containing a vanadium compound and a compound containing at least one metal selected from zirconium, titanium, molybdenum, tungsten, manganese, and cerium and metal surface-treated metal materials. Further, JP No. 2004-183015 A describes metal surface treatment agents containing a vanadium compound and a metal compound containing at least one metal selected from cobalt, nickel, zinc, magnesium, aluminum, etc. and metal surface-treated materials.

Disclosure of the Invention

According to the first aspect of the present invention, there is provided a steel material plated with Zn-containing material and having a composite coating formed therein superior in corrosion resistance, blackening resistance, coating adhesion, and alkali resistance characterized by having a composite coating formed by coating and drying on the surface of a plated steel material a treatment solution containing a basic zirconium compound, vanadyl (VO^{2+}) -containing compound, phosphoric acid compound, cobalt compound, organic acid, and water and having a pH7 to 14, the composite coating containing, with respect to the Zr element as 100 parts by mass, V in an amount of 10 to 45 parts by mass, P in 5 to 100 parts by mass, Co in 0.1 to 20 parts by mass, and an organic acid in 10 to 90 parts by mass.

However, each chromate replacement technology is

insufficient in the corrosion resistance, blackening resistance, and coating adhesion. This is the problem to be solved by the present invention.

5 The inventors engaged in in-depth studies on means for solving the above problem and as a result discovered that by using an aqueous solution of a specific composition to treat a zinc-containing plated steel material, a composite coated zinc-containing plated steel material having superior corrosion resistance, blackening
10 resistance, coating adhesion, and alkali resistance can be obtained and thereby completed the present invention.

That is, the present invention relates to a composite coated zinc-containing plated steel material superior in corrosion resistance, blackening resistance,
15 coating adhesion, and alkali resistance characterized by having a composite coating formed by coating and drying on the surface of a plated steel material a treatment solution containing a basic zirconium compound, vanadyl (VO^{2+})-containing compound, phosphoric acid compound,
20 cobalt compound, organic acid, and water and having a pH7 to 14, the composite coating containing, with respect to the Zr element as 100 mass%, V in an amount of 10 to 45 mass%, P in 5 to 100 mass%, Co in 0.1 to 20 mass%, and an organic acid in 10 to 90 mass%.

25 In the present invention, preferably the composite coating has a total coating mass of 50 to 2000 mg/m^2 . Having a total coating mass of 100 to 1500 mg/m^2 is particularly preferable since it improves the corrosion resistance, blackening resistance, coating adhesion, and
30 alkali resistance.

The composite coated zinc-containing plated steel material according to the present invention has extremely superior performance in each of the corrosion resistance, blackening resistance, coating adhesion, and alkali
35 resistance, so the present invention is an invention having extremely great significance industrially.

BEST MODE FOR CARRYING OUT THE INVENTION

The composite coating in the present invention is formed from a pH7 to 14 treatment solution containing a basic zirconium compound, vanadyl (VO^{2+})-containing compound, phosphoric acid compound, cobalt compound,
5 organic acid, and water.

The basic zirconium compound is a compound supplying the Zr element in the composite coating. The basic zirconium compound is not particularly limited, but for example it may be a zirconium carbonate compound having a
10 cation comprised of $[\text{Zr}(\text{CO}_3)_2(\text{OH})_2]^{2-}$ or $[\text{Zr}(\text{CO}_3)_3(\text{OH})]^{3-}$ or an ammonium salt, potassium salt, sodium salt, etc. containing the cation.

The vanadyl (VO^{2+})-containing compound is a compound supplying the V element in the composite coating. The
15 vanadyl (VO^{2+})-containing compound is not particularly limited, but for example may be a salt between oxovanadium cation and hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid, or other inorganic acid anion or formic acid, acetic acid, propionic acid,
20 butyric acid, oxalic acid, or other organic acid anion. Alternately, a chelate of an organic acid and vanadyl compound, such as vanadyl glycolate, vanadyl dehydroascorbate, may be used.

The composite coating contains the element of V in
25 an amount, with respect to Zr as 100 mass%, of 10 to 45 mass%. If V is less than 10 mass%, the corrosion resistance and the alkali resistance may drop. When V is greater than 45 mass%, the blackening resistance and coating adhesion fall. The amount of V in the composite
30 coating is, with respect to Zr as 100 mass%, preferably 15 to 30 mass%, more preferably 20 to 25 mass%.

The phosphoric acid compound is a compound supplying the P element in the composite coating. The phosphoric
35 acid compound is not particularly limited, but may be phosphoric acid and its ammonium salts etc. More specifically, for example, orthophosphoric acid, pyrophosphoric acid, metaphosphoric acid, polyphosphoric

acid, phytic acid, phosphonic acid, ammonium phosphate, ammonium dihydrogen phosphate, diammonium hydrogen phosphate, sodium phosphate, potassium phosphate, etc. may be mentioned .

5 The composite coating contains the element of P in an amount, with respect to Zr as 100 mass%, of 5 to 100 mass%. If P is less than 5 mass%, the corrosion resistance falls, while if greater than 100 mass%, the blackening resistance, coating adhesion, and alkali
10 resistance fall. The amount of P in the composite coating is, with respect to Zr as 100 mass%, preferably 10 to 70 mass%, more preferably 10 to 40 mass%, particularly preferably 12 to 20 mass%.

 The cobalt compound is a compound supplying the Co
15 element in the composite coating. The cobalt compound is not particularly limited, but for example may be cobalt carbonate, cobalt nitrate, cobalt sulfate, cobalt acetate, etc.

 The composite coating contains the element of Co in
20 an amount, with respect to Zr as 100 mass%, of 0.1 to 20 mass%. If Co is less than 0.1 mass%, the blackening resistance falls, while if Co is greater than 20 mass%, the corrosion resistance, alkali resistance, and coating adhesion fall. In particular, as the effect of the
25 cobalt, this is believed to promote the deactivation of the surface of the plated steel material at the time of formation of the coating and serve to protect the material from water, oxygen, and other external factors. The amount of Co in the composite coating is, with
30 respect to Zr as 100 mass%, preferably 0.5 to 10 mass%, more preferably 0.5 to 5 mass%, particularly preferably 0.8 to 1.5 mass%.

 The composite coating in the present invention also contains an organic acid. The organic acid is not
35 particularly limited, but for example glycolic acid, malic acid, tartaric acid, oxalic acid, citric acid, ascorbic acid, lactic acid, dehydrobenzoic acid,

dehydroascorbic acid, gallic acid, tannic acid, and phytic acid may be mentioned. In some cases, ammonium salts of these organic acids may also be used.

5 The composite coating contains an organic acid in an amount, with respect to Zr as 100 mass%, of 10 to 90 mass%. When the amount of the organic acid is less than 10 mass% with respect to Zr as 100 mass%, the corrosion resistance and the coating adhesion end up deteriorating somewhat. Further, when the treatment solution contains
10 only a little organic acid, the storability of the treatment solution ends up falling. In other words, the organic acid forms a complex with the vanadyl (VO^{2+})-containing compound, basic zirconium compound, and phosphoric acid compound and thereby can maintain the
15 stability of the treatment solution (aqueous solution) for forming the composite coating. If the composite coating contains the organic acid in an amount, with respect to Zr as 100 mass%, of more than 90 mass%, the coating adhesion and the alkali resistance fall. The
20 amount of the organic acid in the composite coating is, with respect to Zr as 100 mass%, preferably 10 to 70 mass%, more preferably 10 to 50 mass%, particularly preferably 15 to 30 mass%.

25 The composite coated zinc-containing plated steel material of the present invention can be produced by coating the surface of a plated steel material with an aqueous solution containing amounts of the basic zirconium compound, vanadyl (VO^{2+})-containing compound, phosphoric acid compound, cobalt compound, and organic
30 acid for supplying the composite coating with the Zr, V, P, and Co elements and organic acid in the above ratios, then heating this to dry and thereby form a coating.

The treatment solution preferably has a pH7 to 14. In this pH range, the basic zirconium compound can be
35 made to stably dissolve in water. As the pH of the treatment solution, 8 to 11 is preferable, while 8 to 10 is particularly preferable. When the pH of the treatment

solution has to be adjusted, as the pH adjuster, the substances shown next may be used. For example, ammonia water, triethylamine, triethanolamine, phosphoric acid, nitric acid, hydrofluoric acid, carbonic acid, ammonium fluoride, etc. may be mentioned, but the pH adjuster is not particularly limited so long as it does not remarkably reduce the stability of the treatment solution.

The coating formed becomes a composite coating having a dense three-dimensional structure, superior in barrier property, and improved in corrosion resistance. One reason why such a composite coating is formed is that the organic acid and metal ions become aligned by formation of a complex, a dense three-dimensional structure is formed mainly by Zr-O, V, organic acid, P, and Co become mixed in the clearances (between mesh structures), and zinc etc. introduced due to etching of the plating surface are introduced. Note that in a dense three-dimensional structure using Zr-O, part of the Zr may be substituted by another element. Further, by etching the plating surface by an organic acid when forming the composite coating, the adhesion at the interface of the coating and plating surface is increased and the corrosion resistance and coating adhesion are improved.

The plated steel material on whose surface the composite coating is formed is not particularly limited so long as the plating layer contains zinc. For example, it is possible to use a plated steel material provided with a plating layer comprised of zinc and unavoidable impurities. Alternatively, it is possible to use a plated steel material provided with a plating layer containing, in addition to zinc (and unavoidable impurities), alloy ingredients with zinc, such as Al, Mg, Si, Ti, Ni, and Fe. A particularly preferable plating layer is one containing, in addition to zinc (and unavoidable impurities), one or more of 60 mass% or less of Al, 10

mass% or less of Mg, and 2 mass% or less of Si.

The plating layer of the plated steel material may be formed by any plating method. For example, the plating layer may be formed by any of hot dip plating, electroplating, vapor deposition plating, dispersion plating, vacuum plating, etc. Further, as the hot dip plating method, there are the flux method, Sendzimir method, method of applying Ni or other preplating to secure wettability, etc. Any of these may be used.

Further, for the purpose of changing the appearance after plating, the plated steel material may be sprayed by water or aerated water, sprayed by a sodium phosphate aqueous solution, or sprayed by zinc powder, zinc phosphate powder, magnesium hydrogen phosphate powder, or an aqueous solution thereof.

Further, to further reinforce the blackening resistance of the plating, as pretreatment for applying the composite coating after the plating, the surface may be prepared by a cobalt sulfate or nickel sulfate solution, etc.

The method of coating the plated steel material surface with the treatment solution may be any of the spray method, dipping method, roll coating method, showering method, air knife method, etc. and is not particularly limited.

When coating the treatment solution, to improve the wettability on the surface of the plated steel material, the treatment solution may be given a surfactant, organic solvent, etc. to a range not impairing its inherent performance. Further, if needed, a defoam agent may also be added.

Further, the treatment solution may be given a lubricant or filler, for example, molybdenum disulfide, graphite, tungsten disulfide, boronitride, graphite fluoride, cerium fluoride, melamine cyanurate, fluoro-resin wax, polyolefin wax, colloidal silica, vapor phase silica, etc. to prevent scratches and wear when

working the composite coated zinc-containing plated steel material of the present invention.

The range of the total coating mass of the composite coating of the plated steel material surface is preferably 50 to 2000 mg/m² or so. In this range, it is possible to obtain the composite coated zinc-containing plated steel material having excellent corrosion resistance, blackening resistance, coating adhesion, and alkali resistance aimed at by the present invention. The particularly preferable range of the total coating amount of the composite coating is 100 to 1500 mg/m². If less than 100 mg/m², the corrosion resistance, blackening resistance, and alkali resistance may drop. If over 1500 mg/m², the coating may become fragile and the alkali resistance and coating adhesion may drop.

When using a treatment solution to treat the plated steel material, the material is preferably heated to dry by a peak metal temperature of 50°C to 200°C in range. Note that the heating method is not particularly limited and may be any of hot air, direct flame, induction heating, infrared rays, an electric oven, etc.

EXAMPLES

Next, the present invention will be explained more specifically, but the present invention is not limited to the following specific examples.

Table 1 shows the ratios of the Zr, V, P, Co, and organic acid of the composite coatings prepared. Note that the compounds used for the treatment solutions are indicated by the following notations:

30 Zr: A1: Zirconium ammonium carbonate
 A2: Zirconium sodium carbonate
 A3: Zirconium potassium carbonate
 V: B1: Vanadyl acetate
 B2: Vanadyl phosphate
35 B3: Vanadyl citrate
 B4: Vanadyl propionate
 P: C1: Ammonium phosphate

C2: Sodium phosphate

Co: D1: Cobalt carbonate

D2: Cobalt nitrate

Organic acids:

5 E1: Citric acid

E2: Maleic acid

E3: Ascorbic acid

E4: Adipic acid

10 Note that as comparative conditions, the following prior arts were used.

Prior Art 1:

A composite coating formed from a treatment solution containing Zr, V, and P, not containing Co, and containing dimercaptosuccinic acid.

15 Prior Art 2:

A composite coating formed from a treatment solution containing Zr and V and not containing P, Co, and an organic acid.

Prior Art 3:

20 A composite coating formed from a treatment solution containing Zr, V, P, Co, and an organic acid but having ratios of V and organic acid with respect to Zr as 100 mass% outside the scope of the present invention (both V and organic acid being greater in amounts).

25 Prior Art 4:

A coating formed using as a coating type chromate treatment solution a mixed solution of a partially reduced chromic acid aqueous solution (reduction rate 40%) and colloidal silica ($\text{CrO}_3:\text{SiO}_2=1:3$).

30 The composite coating was prepared by coating a treatment solution diluted by deionized water to adjust the ingredients to predetermined concentrations on the surface of a plated steel material by a roll coater to give a predetermined dried coating amount and immediately
35 using a hot air dryer to heat and dry the coating at a peak metal temperature of 80°C. The treatment solution had a pH of 9.

Table 2 shows the treatment conditions and results of tests and evaluation of the fabricated test pieces. The plated steel materials used have the following notations.

- 5 M1: Hot dip Zn plating (plating deposition 90 mg/m²)
M2: Hot dip 11%Al-3%Mg-0.2%Si-Zn plating
(plating deposition 90 mg/m²)
M3: Electro-Zn plating (plating deposition 20 mg/m²)
M4: Electro-11%Ni-Zn plating (plating deposition 20
10 mg/m²)
M5: Hot dip 55%Al-1.6%Si-Zn plating
(plating deposition 90 mg/m²)

Below, the evaluation items and test methods will be shown.

15 - Corrosion Resistance

Sheet and cross-cut test pieces were subjected to salt spray tests based on JIS Z 2371 for 240 hours. The corrosion resistance was judged by the area percentage of white rust after the salt spray test.

20 The evaluation criteria for the corrosion resistance are as follows:

Sheet test piece:

- A: White rust 0%
B: White rust over 0% and not more than 5%
25 C: White rust over 5% and not more than 30%
D: White rust over 30%

Cross-cut test piece (including white rust at cut parts and vicinities)

- A: White rust 0%
30 B: White rust over 0% and not more than 5%
C: White rust over 5% and not more than 30%
D: White rust over 30%

- Alkali Resistance

- 20 g/L of Parclean® N364S (made by Nihon
35 Parkerizing) was sprayed on the sheet test piece at 60°C for 30 seconds by a spray pressure of 50 kPa. Thereafter, the test piece was washed by tap water for 10 seconds,

then dried by cool air. Next, in the same way as above, this was subjected to a salt spray test for 240 hours and judged for the area percentage of white rust after the salt spray test.

- 5 The evaluation criteria for the alkali resistance are shown below:

- A: White rust 0%
- B: White rust over 0% and not more than 5%
- C: White rust over 5% and not more than 30%
- 10 D: White rust over 30%

- Blackening Resistance

- Using a constant temperature and constant humidity test, a test piece was allowed to stand in a 70°C x RH85% atmosphere for 144 hours, then the appearance was
15 visually examined.

 The evaluation criteria for the blackening resistance are shown below:

- A: No change at all
- B: Almost no change observed
- 20 C: Some discoloration observed
- D: Clear discoloration observed

- Coating Adhesion

- A test piece was coated with Amilac 1000 White® (made by Kansai Paint) using a bar coater and was heated
25 to dry at 120°C for 20 minutes to obtain a 20 µm dried thickness. Next, it was immersed in boiling water for 30 minutes, taken out, then allowed to naturally stand for 24 hours. Thereafter, a cutter knife was used to cut the coating into a checkerboard of 100 1-mm squares and a
30 tape peeling test was used to find the remaining number of coating squares.

 The evaluation criteria for the coating adhesion are shown below:

- A: Remaining squares 100
- 35 B: Remaining squares 98 to less than 100
- C: Remaining squares 50 to less than 98

D: Remaining squares less than 50

Table 1. Mass% of Ingredients in Composite Coating

Composition of composite coating ("Compound" is a compound used for treatment solution)															Remarks
Composite Coating		Zr		V		P		Co		Organic acid		Other			
		Compound	mass%	Compound	mass%	Compound	mass%	Compound	mass%	Compound	mass%				
Composite Coating 1	Al	100	B1	10	C1	15	D1	1	E1	20				Invention	
Composite Coating 2	Al	100	B1	45	C1	15	D1	1	E1	20				Invention	
Composite Coating 3	Al	100	B1	25	C1	5	D1	1	E1	20				Invention	
Composite Coating 4	Al	100	B1	20	C1	100	D1	1	E1	20				Invention	
Composite Coating 5	Al	100	B1	20	C1	15	D1	0.1	E1	20				Invention	
Composite Coating 6	Al	100	B1	20	C1	15	D1	20	E1	20				Invention	
Composite Coating 7	Al	100	B1	20	C1	15	D1	1	E1	10				Invention	
Composite Coating 8	Al	100	B1	20	C1	15	D1	1	E1	90				Invention	
Composite Coating 9	A2	100	B1	20	C1	15	D1	1	E1	20				Invention	
Composite Coating 10	A3	100	B1	20	C1	15	D1	1	E1	20				Invention	
Composite Coating 11	Al	100	B2	20	C1	15	D1	1	E1	20				Invention	
Composite Coating 12	Al	100	B3	20	C1	15	D1	1	E1	20				Invention	
Composite Coating 13	Al	100	B4	20	C1	15	D1	1	E1	20				Invention	
Composite Coating 14	Al	100	B1	20	C2	15	D1	1	E1	20				Invention	
Composite Coating 15	Al	100	B1	20	C1	15	D2	1	E1	20				Invention	
Composite Coating 16	Al	100	B1	20	C1	15	D1	1	E2	20				Invention	
Composite Coating 17	Al	100	B1	20	C1	15	D1	1	E3	20				Invention	
Composite Coating 18	Al	100	B1	20	C1	15	D1	1	E4	20				Invention	
Composite Coating 19	Al	100	B1	5	C1	15	D1	1	E1	20				Comp. Ex.	
Composite Coating 20	Al	100	B1	50	C1	15	D1	1	E1	20				Comp. Ex.	
Composite Coating 21	Al	100	B1	20	C1	2.5	D1	1	E1	20				Comp. Ex.	
Composite Coating 22	Al	100	B1	20	C1	150	D1	1	E1	20				Comp. Ex.	
Composite Coating 23	Al	100	B1	20	C1	15	D1	0.05	E1	20				Comp. Ex.	
Composite Coating 24	Al	100	B1	20	C1	15	D1	40	E1	20				Comp. Ex.	
Composite Coating 25	Al	100	B1	20	C1	15	D1	1	E1	5				Comp. Ex.	
Composite Coating 26	Al	100	B1	20	C1	15	D1	1	E1	150				Comp. Ex.	
Prior Art 1	Al	100	B1	50	C1	20	-	-	E1	50		0.5 (dimethylcaptosuccinic acid)		Comp. Ex.	
Prior Art 2	Al	100	B1	50	-	-	-	-	-	-				Comp. Ex.	
Prior Art 3	Al	100	B1	100	C1	8	D1	3	E1	100				Comp. Ex.	
Prior Art 4														Comp. Ex.	
														Comp. Ex.	

Coating type chromate

Table 2. Results of Evaluation

		Treatment conditions				Corrosion resistance		Blackening resistance	Coating adhesion	Remarks
		Plated steel mat.	Composite coating	Total coating (mg/m ²)	Sheet	Cross-cut				
Ex. 1	M1	Composite Coating 1	500	A	A	A	A	A	Invention	
Ex. 2	M1	Composite Coating 2	500	A	A	A	A	A	Invention	
Ex. 3	M1	Composite Coating 3	500	A	A	A	A	A	Invention	
Ex. 4	M1	Composite Coating 4	500	A	A	A	A	A	Invention	
Ex. 5	M1	Composite Coating 5	500	A	A	A	A	A	Invention	
Ex. 6	M1	Composite Coating 6	500	A	A	A	A	A	Invention	
Ex. 7	M1	Composite Coating 7	500	A	A	A	A	A	Invention	
Ex. 8	M1	Composite Coating 8	500	A	A	A	A	A	Invention	
Ex. 9	M1	Composite Coating 9	500	A	A	A	A	A	Invention	
Ex. 10	M1	Composite Coating 10	500	A	A	A	A	A	Invention	
Ex. 11	M1	Composite Coating 11	500	A	A	A	A	A	Invention	
Ex. 12	M1	Composite Coating 12	500	A	A	A	A	A	Invention	
Ex. 13	M1	Composite Coating 13	500	A	A	A	A	A	Invention	
Ex. 14	M1	Composite Coating 14	500	A	A	A	A	A	Invention	
Ex. 15	M1	Composite Coating 15	500	A	A	A	A	A	Invention	
Ex. 16	M1	Composite Coating 16	500	A	A	A	A	A	Invention	
Ex. 17	M1	Composite Coating 17	500	A	A	A	A	A	Invention	
Ex. 18	M1	Composite Coating 18	500	A	A	A	A	A	Invention	
Ex. 19	M2	Composite Coating 1	500	A	A	A	A	A	Invention	
Ex. 20	M3	Composite Coating 1	500	A	A	A	A	A	Invention	
Ex. 21	M4	Composite Coating 1	500	A	A	A	A	A	Invention	
Ex. 22	M5	Composite Coating 1	500	A	A	A	A	A	Invention	
Ex. 23	M1	Composite Coating 1	50	B	B	B	B	B	Invention	
Ex. 24	M1	Composite Coating 1	100	A	A	A	A	A	Invention	
Ex. 25	M1	Composite Coating 1	1500	A	A	A	A	A	Invention	
Ex. 26	M1	Composite Coating 1	2000	A	A	A	A	A	Invention	
Ex. 27	M2	Composite Coating 1	50	B	B	B	B	B	Invention	
Ex. 28	M2	Composite Coating 1	100	A	A	A	A	A	Invention	
Ex. 29	M2	Composite Coating 1	1500	A	A	A	A	A	Invention	
Ex. 30	M2	Composite Coating 1	2000	A	A	A	A	A	Invention	
Comp. Ex. 1	M1	Composite Coating 19	500	C	C	C	C	C	Comp. Ex.	
Comp. Ex. 2	M1	Composite Coating 20	500	B	B	B	B	B	Comp. Ex.	
Comp. Ex. 3	M1	Composite Coating 21	500	C	C	C	C	C	Comp. Ex.	
Comp. Ex. 4	M1	Composite Coating 22	500	B	B	B	B	B	Comp. Ex.	
Comp. Ex. 5	M1	Composite Coating 23	500	B	B	B	B	B	Comp. Ex.	
Comp. Ex. 6	M1	Composite Coating 24	500	C	C	C	C	C	Comp. Ex.	
Comp. Ex. 7	M1	Composite Coating 25	500	C	C	C	C	C	Comp. Ex.	
Comp. Ex. 8	M1	Composite Coating 26	500	B	B	B	B	B	Comp. Ex.	
Comp. Ex. 9	M2	Prior Art 1	500	B	B	B	B	B	Comp. Ex.	
Comp. Ex. 10	M2	Prior Art 2	500	C	D	D	D	D	Comp. Ex.	
Comp. Ex. 11	M2	Prior Art 3	500	B	B	B	B	B	Comp. Ex.	
Comp. Ex. 12	M1	Prior Art 4	500	C	C	C	C	C	Comp. Ex.	

As shown in Table 2, the composite coated zinc-containing plated steel material according to the present invention clearly has superior performance in each of the corrosion resistance (evaluation by sheet test piece and cross-cut test piece), blackening resistance, coating adhesion, and alkali resistance. In particular, in test pieces with a composite coating of a total coating mass of 100 to 1500 mg/m², superior results were exhibited for all of the evaluated corrosion resistance, blackening resistance, coating adhesion, and alkali resistance. As opposed to this, in the plated steel materials of the comparative examples, there were no examples able to satisfy all of the performances of corrosion resistance, blackening resistance, coating adhesion, and alkali resistance.

The claims defining the invention are as follows:

1. A steel material plated with Zn-containing material and having a composite coating formed therein superior in corrosion resistance, blackening resistance, coating adhesion, and alkali resistance characterized by having a composite coating formed by coating and drying on the surface of a plated steel material a treatment solution containing a basic zirconium compound, vanadyl (VO^{2+}) -containing compound, phosphoric acid compound, cobalt compound, organic acid, and water and having a pH7 to 14, the composite coating containing, with respect to the Zr element as 100 parts by mass, V in an amount of 10 to 45 parts by mass, P in 5 to 100 parts by mass, Co in 0.1 to 20 parts by mass, and an organic acid in 10 to 90 parts by mass.
2. A steel material plated with Zn-containing material and having a composite coating formed therein superior in corrosion resistance, blackening resistance, coating adhesion, and alkali resistance as set forth in claim 1, wherein said composite coating has a total coating mass of 50 to 2000 mg/m².
3. A steel material plated with Zn-containing material and having a composite coating formed therein superior in corrosion resistance, blackening resistance, coating adhesion, and alkali resistance as set forth in claim 2, wherein said composite coating has a total coating mass of 100 to 1500 mg/m².
4. A steel material plated with Zn-containing material and having a composite coating formed therein superior in corrosion resistance, blackening resistance, coating adhesion, and alkali resistance as set forth in any one of claims 1 to 3 wherein the plated steel material has a plating layer comprised of a composition of Zn and unavoidable impurities.
5. A steel material plated with Zn-containing material and having a composite coating formed therein superior in corrosion resistance, blackening resistance, coating adhesion, and alkali resistance as set forth in any one of claims 1 to 3 wherein the plated steel material has a plating layer comprised of a composition containing, in addition to zinc and unavoidable impurities, one or more of 60 mass% or less of Al, 10 mass% or less of Mg, and 2 mass% or less of Si.

6. A steel material plated with Zn-containing material and having a composite coating formed therein, substantially as hereinbefore described with reference to any one of the examples but excluding any one of the comparative examples.